

Rovibrationally-Resolved Photodissociation of SH^+

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Abstract. Photodissociation cross sections for the SH^+ radical are computed from all rovibrational (RV) levels of the ground electronic state $X^3\Sigma^-$ for wavelengths from threshold to 500 Å. The five electronic transitions, $2^3\Sigma^- \leftarrow X^3\Sigma^-$, $3^3\Sigma^- \leftarrow X^3\Sigma^-$, $A^3\Pi \leftarrow X^3\Sigma^-$, $2^3\Pi \leftarrow X^3\Sigma^-$, and $3^3\Pi \leftarrow X^3\Sigma^-$, are treated with a fully quantum-mechanical two-state model, i.e. no non-adiabatic coupling between excited states was included in our work. The photodissociation calculations incorporate adiabatic potentials and transition dipole moment functions computed in the multireference configuration interaction approach along with the Davidson correction (MRCI+Q), but adjusted to match available experimental molecular data and asymptotic atomic limits. Local thermodynamic equilibrium (LTE) photodissociation cross sections were computed which assume a Boltzmann distribution of RV levels in the $X^3\Sigma^-$ molecular state of the SH^+ cation. The LTE cross sections are presented for temperatures in the range 1000-10,000 K. Applications of the current photodissociation cross sections to interstellar gas, photon-dominated regions, and stellar atmospheres are briefly discussed.

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1. Introduction

In the search for novel molecular species in interstellar and circumstellar environments, many sulfur-containing molecules have been observed and identified in diffuse, translucent, and dense clouds [1, 2]. The sulfur-bearing molecules SH and SH^+ have recently been observed in the interstellar medium (ISM) [3, 4]. In particular, the SH^+ 526 GHz transition was detected in emission using the *Herschel* infrared space observatory toward the high-mass protostar W3 IRS 5 [4] and in the diffuse ISM of distant star-forming regions [5]. Towards Sgr B2(M), the 638 GHz transition of SH^+ has also been detected in absorption using the Carbon Heterodyne Array of the MPIfR (CHAMP+) receiver of the Atacama Pathfinder Experiment 12 m telescope [6]. SH and SH^+ facilitate the formation of other sulfur-bearing molecules, so information about their abundances is relevant for the investigation of the chemical composition of astrophysical environments. As searches for new molecular species continue, molecular formation and destruction processes involving sulfur are of considerable interest. These molecular reactions, along with other processes, can be used to create a chemical network that can predict the concentrations of major sulfur species in various astrophysical environments [1, 2, 7, 8]. One such process is photodissociation, an important mechanism for the destruction of molecules in the ISM. For example, the sulfur hydride ion may be dissociated by



The surviving SH^+ enables the formation of other sulfur-bearing molecules, including SH and H_nS^+ . In the ISM, SH^+ forms through an endothermic reaction of H_2 and S^+ ,



and through radiative association



[9]. For the endothermic reaction, state-to-state formation rates are not available, so the UMIST estimations based on CH^+ are often adopted. This assumption is reasonable because SH^+ forms via a similar reaction for CH^+ and the total rates of the reactions for CH^+ and SH^+ formation through these processes are expected to be of the same order of magnitude. This endothermic reaction requires the passage of a shock, specifically a magnetohydrodynamic shock, due to an activation barrier of 9960 K. The endothermicity of this reaction likely contributes to the difficulty of detection of SH^+ in the ISM. In many environments, such as photon-dominated regions (PDRs), SH^+ does not react with H_2 at the given physical conditions resulting in a reaction rate orders of magnitude lower than that of reactions with electrons and H. Consequently, photodissociation and the reactions with H and electrons dominant SH^+ destruction [10].

Using ab initio molecular potential energies and transition dipole moment functions in a quantum-mechanical scattering formalism, we have carried out the first calculations for the photodissociation of SH^+ . These computed photodissociation cross sections can be used to obtain local photo-rates which can then be folded into chemical network models to improve the sulfur chemistry. In particular, the cross sections have been computed for five transitions to the lowest-lying electronic states from 841 rovibrational (RV) levels of the $\text{X } ^3\Sigma^-$ electronic ground state. Cross sections for thermal populations of RV levels are also obtained and astrophysical applications of the current results are briefly discussed.

2. Theory

2.1. Electronic Structure

Following early work on this molecular cation [9] for radiative association, and our most recent study on radiative charge transfer [11], we use our accurate results (obtained from a parallel version of the MOLPRO [12] suite of *ab initio* quantum chemistry codes, release MOLPRO 2010) for potential energies and transition dipole moments (TDMs), as well as additional TDMs, to study photodissociation of this cation from all RV levels. The potential energies curves and transition dipole moments were obtained as a function of bond length out to a bond separation of $R = 20 \text{ a}_0$. For internuclear separations beyond this, we use a multipole expansion to represent the long-range part of the potentials.

We have previously outlined in detail the molecular structure calculations [11] so here we just give a brief outline. We conducted multi-reference configuration interaction using the internally contracted MRCI method available in the MOLPRO quantum chemistry suite of codes. The orbitals used in this procedure were obtained from the State-Averaged Multi-Configuration-Self-Consistent-Field (SA-MCSCF) method [13]. The Davidson correction (referred to as Q) was applied to all our results [14]. In our work the core orbitals are optimised and the valence orbitals are correlated at the CASSCF level.

For the SH^+ cation, the natural Abelian symmetry group is $C_{\infty v}$ but due to the limitation of the Gaussian orbitals code MOLPRO, our electronic structure computations were performed in the reduced Abelian symmetry group C_{2v} i.e. (A_1 , B_1 , B_2 , A_2). When the symmetry is reduced from $C_{\infty v}$ to C_{2v} , the correlating relationships are $\sigma \rightarrow a_1$, $\pi \rightarrow (b_1, b_2)$, $\delta \rightarrow (a_1, a_2)$. The active space consists of 16 electrons and 10 molecular orbitals ($6a_1, 2b_1, 2b_2, 0a_2$) i.e., a (6, 2, 2, 0) active space. To take account of short-range interactions we employed the multi-configuration-self-consistent-field (MCSCF) method [15, 16] available within the MOLPRO [12] suite of codes. This procedure simultaneously optimises molecular orbitals and coefficients providing a truer representation of the molecular states. The averaging process was carried out on the lowest four $^3\Pi$, three $^3\Sigma^-$ and three $^3\Delta$ molecular states.

In Fig. 1(a) we illustrate all the triplet states involved in the photodissociation processes. All the potential energies in Fig. 1 are given in eV relative to the ground-state equilibrium bond distance r_e . Table 1 gives asymptotic properties of the molecular states. Fig. 1(b) illustrates the dipole transition moments $D(R)$ as a function of internuclear separation R connecting the $X \ ^3\Sigma^-$ to the excited triplet electronic states involved in the dynamics. We note that the asymptotic separated-atom energies in the MRCI+Q approximation show suitable agreement with experimental atomic values (see Table 1). Our results show smooth transition dipole moments connecting all of the adiabatic triplet states which leads us to conclude that the sensitivity of the transitions will be primarily due to the RV wave function envelope. Resonance behaviour can be expected to be primarily due to potential scattering in the outgoing dissociation channel.

Beyond $R = 20 \text{ a}_0$, the potential energies of the $3 \ ^3\Sigma^-$ and $3 \ ^3\Pi$ excited states can be approximated by the long-range multipole expansion,

$$V(R) = \frac{Q_M}{2R^3} - \frac{\alpha_d}{2R^4} + V(R \rightarrow +\infty), \quad (4)$$

where Q_M is the quadrupole moment and α_d is the dipole polarizability of the neutral

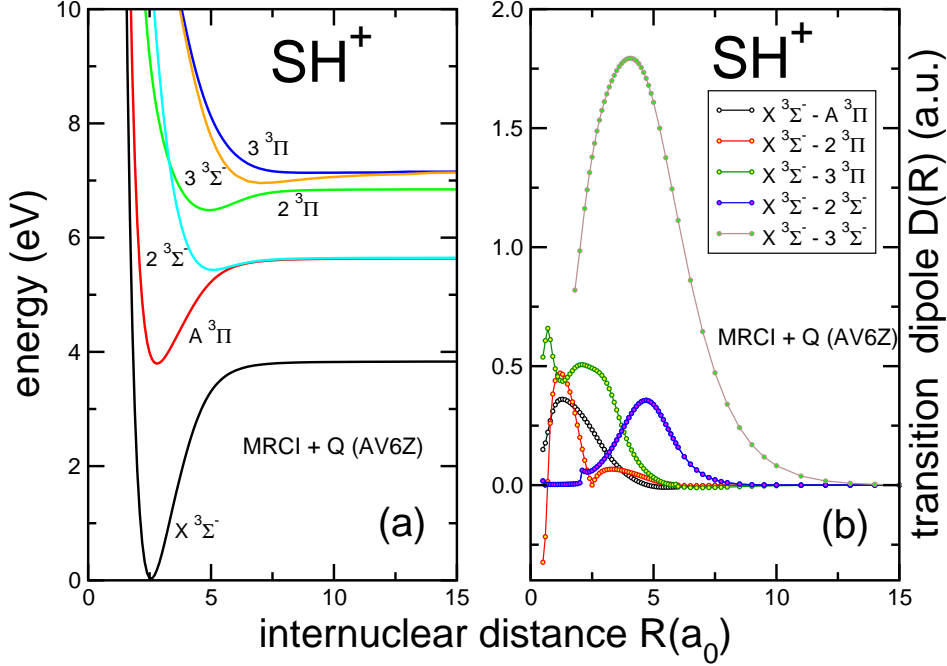


Figure 1. (a) Relative electronic energies (eV) for the SH^+ molecular cation, as a function of bond separation at the MRCI+Q level of approximation with an AV6Z basis. Energies are relative to the ground state near equilibrium ($2.6 a_0$). The states shown are for the transitions connecting the $X^3\Sigma^- \rightarrow 2^3\Sigma^-$, $3^3\Sigma^-$, $A^3\Pi$, $2^3\Pi$, $3^3\Pi$ states involved in the photodissociation process. (b) Dipole transition moments $D(R)$ (a.u.) for the $X^3\Sigma^- \rightarrow A^3\Pi$, $2^3\Sigma^-$, $3^3\Sigma^-$, $2^3\Pi$, $3^3\Pi$, transitions. The MRCI + Q approximation with an AV6Z basis set was used to calculate the transition dipole moments.

atom. Q_M for a p^4 configuration is $-\frac{4}{5}e \langle r^2 \rangle$ for a Σ state and $\frac{2}{5}e \langle r^2 \rangle$ for a Π state [17], where the $\langle r^2 \rangle$ value for sulfur is 5.065255 a.u. ($3P$ state) [18, 19] and $Q_M = 0$ for H. The atomic values for the dipole polarizability adopted here are respectively, $\alpha(\text{S})=18.0$ and $\alpha(\text{H})=4.5$ from the early work of Miller and Bederson [20]. The long-range expansion of the ground and other excited electronic states includes just the last 2 terms of the right hand side in (4), i.e. $Q_M = 0$. At short range internuclear distances, we fitted the potentials with the form,

$$V = Ae^{-BR} + C, \quad (5)$$

where A , B and C are fitting coefficients. A similar approach was used for the TDMs to extend to long and short range internuclear distances. Since our TDM's data are computed on the grid (R_{min}, R_{max}) , so for $R < R_{min}$ a quadratic form

$$V = aR^2 + bR + c, \quad (6)$$

was used to connect to the united atom limit. Similarly for $R > R_{max}$ we used the

Table 1. The asymptotic separated-atom (SA) and the united-atom (UA) limits for the molecular states involved in the SH^+ photodissociation process. Energies E (eV) are relative to the separated atom for the ground state.

Molecular State	Separated-atom Atomic state	E (eV) Expt. ^a	E (eV) Theory ^b	ΔE (eV)	United-atom Cl^+ Atomic state	Cl^+ TDM's ^c (a.u.)
X $^3\Sigma^-$	$S^+(3s^2 3p^3 \ ^4S^o) + H(^2S)$	0.0	0.0	-	$3s^2 3p^4 \ ^3P$	-
A $^3\Pi$	$S^+(3s^2 3p^3 \ ^2D^o) + H(^2S)$	1.8439	1.8066	+0.0373	$3s^2 3p^4 \ ^3P$	0.0
2 $^3\Sigma^-$	$S^+(3s^2 3p^3 \ ^2D^o) + H(^2S)$	1.8439	1.8177	+0.0262	$3s^2 3p^3 ({}^4S^o) 4s \ ^3S^o$	unknown
2 $^3\Pi$	$S^+(3s^2 3p^3 \ ^2P^o) + H(^2S)$	3.0445	3.0150	+0.0295	$3s 3p^5 \ ^3P^o$	0.459
3 $^3\Sigma^-$	$S(3s^2 3p^4 \ ^3P) + H^+(^1S)$	3.2384	3.3321	-0.0937	$3s^2 3p^3 ({}^4S^o) 3d \ ^3D^o$	0.997
3 $^3\Pi$	$S(3s^2 3p^4 \ ^3P) + H^+(^1S)$	3.2384	3.3569	-0.1185	$3s^2 3p^3 ({}^4S^o) 3d \ ^3D^o$	0.997

^aEnergy values deduced from the NIST Atomic Spectra Database tabulations [22].

^bEnergy values from MOLPRO [12], MRCI+Q approximation (AV6Z basis).

^cTransition dipole moments (TDM's) with initial states, deduced from [22, 23].

functional form,

$$V = a'e^{-b'R} + c', \quad (7)$$

to connect to the separated atom limit. The reduced mass used in our work was for the most abundant species and taken from the compilation of Huber and Herzberg [21].

2.2. Photodissociation Approach

The direct photodissociation rate due to absorption from the initial RV level is

$$k_{fi}^{pd} = \int \sigma^{fi}(\lambda) I(\lambda) d\lambda s^{-1}, \quad (8)$$

where $\sigma^{fi}(\lambda)$ is the direct photodissociation cross section for absorption into the RV continuum of electronic state f and I is the mean intensity of the radiation field. Given that the radiation field in most environments is unknown, we focus in this work on the cross section, which for a bound-free transition from initial state i to final state f for an electric dipole transition, can be expressed as [24]

$$\sigma^{fi}(E_{ph}) = \frac{2\pi^2 e^2 \hbar}{m_e c} \frac{df}{dE_{ph}}, \quad (9)$$

where m_e is the mass of the electron, E_{ph} is the photon energy, and the other constants have their usual meanings. Eq. (9) can be written as

$$\sigma^{fi}(E_{ph}) = \frac{4\pi^2}{3} \alpha E_{ph} |\langle \Phi_f(\vec{r}, \vec{R}) | \vec{r} | \Phi_i(\vec{r}, \vec{R}) \rangle|^2, \quad (10)$$

when we used the continuum differential oscillator strength and the definition of the fine-structure constant, $\alpha = e^2/\hbar c$. The continuum differential oscillator strength in the length gauge is given as

$$\frac{df}{dE_{ph}} = \frac{2m_e}{3\hbar^2} E_{ph} |\langle \Phi_f(\vec{r}, \vec{R}) | \vec{r} | \Phi_i(\vec{r}, \vec{R}) \rangle|^2, \quad (11)$$

where $\Phi(\vec{r}, \vec{R})$ is the total molecular wave function, \vec{r} is the electronic coordinate vector, and \vec{R} is the internuclear vector. The numerical value of the pre-factor becomes 2.689×10^{-18} when all quantities in Eq. (10) are taken in atomic units, and the cross

section is expressed in cm^2 . By applying separation of variables to the electronic and nuclear coordinates of Φ , the electric dipole transition moment function becomes

$$D^{fi}(R) = \langle \phi_f(\vec{r}|R) | \vec{r} | \phi_i(\vec{r}|R) \rangle, \quad (12)$$

where $\phi(\vec{r}|R)$ is the electronic molecular wave function for fixed R and integration is taken over all electronic coordinates. Then, the photodissociation cross section from initial rovibrational level $v''J''$ can be expressed as [25]

$$\begin{aligned} \sigma_{v''J''}^{fi}(E_{\text{ph}}) &= 2.689 \times 10^{-18} E_{\text{ph}} g \\ &\times \sum_{J'} \left(\frac{1}{2J'' + 1} S_{J'} |D_{k'J',v''J''}^{fi}|^2 \right) \text{cm}^2, \end{aligned} \quad (13)$$

where the Hönl-London factors, $S_{J'}(J'')$ for a $\Sigma \leftarrow \Sigma$ electronic transition are given by

$$S_{J'}(J'') = \begin{cases} J'' - 1, & J' = J'' - 1 \text{ (P-branch)} \\ J'' + 1, & J' = J'' + 1 \text{ (R-branch)}, \end{cases} \quad (14)$$

and for a $\Pi \leftarrow \Sigma$ electronic transition are written as

$$S_{J'}(J'') = \begin{cases} (J'' - 1)/2, & J' = J'' - 1 \text{ (P-branch)} \\ (2J'' + 1)/2, & J' = J'' \text{ (Q-branch)} \\ (J'' + 1)/2, & J' = J'' + 1 \text{ (R-branch)}. \end{cases} \quad (15)$$

The matrix element of the electric dipole transition moment for absorption from the rovibrational level $v''J''$ in state i to the continuum $k'J'$ in state f is $D_{k'J',v''J''}^{fi} = \langle \chi_{k'J'}(R) | D^{fi}(R) | \chi_{v''J''}(R) \rangle$ where J is the angular momentum of nuclear motion and g is the degeneracy factor, with the integration taken over R . The degeneracy factor is written as

$$g = \frac{2 - \delta_{0,\Lambda' + \Lambda''}}{2 - \delta_{0,\Lambda''}}, \quad (16)$$

where Λ' and Λ'' are the angular momenta projected along the nuclear axis for the final and initial electronic states. The bound and continuum rovibrational wave functions, $\chi_{v''J''}(R)$ and $\chi_{k'J'}(R)$ are solutions of the radial Schrödinger equation for nuclear motion on the i and f state potential curves. The continuum wave functions are normalized such that they behave asymptotically as

$$\chi_{k'J'}(R) = \left(\frac{2\mu}{\pi^2 E'} \right)^{1/4} \sin(k'R - \frac{\pi}{2}J' + \eta_{J'}), \quad (17)$$

where μ is the molecular reduced mass [21], $\eta_{J'}$ the phase shift, E' the center-of-mass kinetic energy for the free particles, and the wave vector is given by $k' = \sqrt{2\mu E'}$. The wave functions were obtained numerically using the standard Numerov method [26, 27, 28] with a step size of 0.001 a_0 over internuclear distances $0.1 < R < 200 a_0$.

If the density of the environment is sufficiently high, then the populations of the $v''J''$ levels may be assumed to be thermalized and it is appropriate to consider the so-called local thermodynamic equilibrium (LTE) cross section,

$$\begin{aligned} \sigma(\lambda, T) &= \frac{1}{Q(T)} \sum_{v''} \sum_{J''} (2J'' + 1) \exp[-(E_{v''=0, J''=0} - E_{v''J''})/k_b T] \\ &\times \sigma_{v''J''}(\lambda), \end{aligned} \quad (18)$$

[29], which depends only on the gas temperature T and the photon wavelength λ where k_b is Boltzmann's constant, with the RV partition function given by

$$Q(T) = \sum_{v''} \sum_{J''} (2J'' + 1) \exp[-(E_{v''=0, J''=0} - E_{v''J''})/k_b T]. \quad (19)$$

Table 2. Spectroscopic constants for the $X^3\Sigma^-$ electronic ground state compared to available experimental and theoretical data.

r_e (a ₀)	D_e (eV)	D_0^0 (eV)	ω_e (cm ⁻¹)	$\omega_e x_e$ (cm ⁻¹)	Notes
2.56	3.843	3.684	2601.1	54.1	This work
2.577	-	-	2558.0	0	Ref. [30]
2.597	-	3.48	2547.7	49.3	Ref. [21]
2.572	-	3.488	2555.2	49.0	Ref. [31]

3. Results and Discussion

3.1. Spectroscopic Properties

Using the ab initio data for the $X^3\Sigma^-$ potential described above, we obtained the spectroscopic constants given in Table 2. This is compared to experimental data [21, 30] and the previous theoretical results of Khadri et al. [31] and found to be in reasonable agreement. The $X^3\Sigma^-$ is found to support 22 vibrational levels, with a maximum rotational level $J'' = 62$, for a total of 841 rovibrational levels.

3.2. Partial cross sections for rovibrationally-resolved photodissociation

A selection of the partial cross sections $\sigma_{v'',J''}$ for the $2^3\Sigma^- \leftarrow X^3\Sigma^-$ transition as a function of the photon wavelength are presented in Figure 2 with results for $v'' = 0$ and select J'' given in Figure 2a and $v'' = 15$ in Figure 2b. As expected the cross sections migrate to larger photon energies due to the decreasing photon threshold energy with increasing v'' and/or J'' . Orbiting resonances due to quasi-bound levels in the upper state become evident near threshold for relatively large v'' and/or J'' . The same trends are evident for the other four electronic transitions give in Figures 3-6. Of note, is the $A^3\Pi \leftarrow X^3\Sigma^-$ transition, which has a very weak cross from $v'' = 0$, $J'' = 0$ due to the fact the most of the oscillator strength resides in bound-bound transitions as opposed to the bound-free case. However, the cross sections become significant, comparable to other electronic transitions, for large v'' and/or J'' , but also at wavelengths longer than ~ 2000 Å.

Figure 7 compares the cross sections for each transition from the electronic and rovibrational ground-state $v'' = 0$, $J'' = 0$ which is relevant for cold to warm interstellar diffuse and translucent clouds. The $3^3\Sigma^- \leftarrow X^3\Sigma^-$ and $3^3\Pi \leftarrow X^3\Sigma^-$ dominate with most of their cross section falling between the H Lyman photoionization limit and the H Lyman α being the region where the ISM radiation field is most intense. The other transitions are at least two orders of magnitude weaker with their peaks lying at longer wavelengths.

As far as we are aware, the current work is the first explicit photodissociation calculations for the SH^+ radical ion. An estimate was made in van Dishoeck et al. [32] of the SH^+ cross section by scaling that of CH^+ . As illustrated in Figure 7, there is suitable agreement, however the current results are about a factor of 3 larger, therefore we would expect the photodissociation rate to be enhanced by a similar amount.

3.3. LTE photodissociation cross sections

Figures 8-12 present the LTE cross sections, which assume a thermal population for the RV levels in $\text{X } ^3\Sigma^-$, for all five transitions. The LTE cross sections are shown for plasmas temperatures in the range from 1000 to 10,000 K and indicate two main features: i) cross sections at longer wavelength increase with increasing temperature and ii) cross sections at the peak for $v'' = 0$, $J'' = 0$ typically decrease as shown in Figure 8. However, the overall difference between the RV ground state cross section and that for 1000 K is not large.

In Figure 13, the LTE cross sections for all five transitions are compared at 3000 K. This should be compared to Figure 7 for $v'' = 0$, $J'' = 0$ where it is seen that the cross sections are larger in the LTE case for wavelengths longer than $\sim 1500 \text{ \AA}$. In particular, the $\text{A } ^3\Pi \leftarrow \text{X } ^3\Sigma^-$ transition, which is negligible for $v'' = 0$, $J'' = 0$ results in a large LTE cross section peak, dominating all other transitions, near 2800 \AA .

4. Astrophysical Applications

The SH^+ radical ion, sulfanylium, was not detected in the ISM until as late as 2010 [4]. It is however, an important tracer of gas condensations in dense regions and also probes the warm surface layers of PDRs [10]. Furthermore, its abundance is expected to be enhanced in X-ray dominated regions (XDRs) [33]. In their model of the Orion Bar PDR, Nagy et al. [10] find that photodissociation accounts for a maximum of about 4.4% of the total destruction rate of SH^+ , since reactive collisions with H and dissociative recombination by electrons are more efficient. However, they adopted the estimated cross section of Ref. [32] for $v'' = 0$, $J'' = 0$. We point out that the adoption of the current cross sections would enhance the photodissociation contribution to greater than 10%. We note that the photodissociation rates are not given here as they are sensitive to the local radiation field and dust properties. The latter is quite different in the Orion Bar from the average ISM of the galaxy. The densities and temperatures (10^5 - 10^6 cm^{-3} and $\sim 1000 \text{ K}$) of the Orion Bar PDR begin to approach the regime where photodissociation from excited states might contribute which is currently neglected in all models. Furthermore, LTE conditions are almost satisfied, but at 1000 K there is not a significant difference between the LTE and $v'' = 0$, $J'' = 0$ cross sections

For higher density and temperature environments, such as proto-planetary discs (PPDs) and planetary and stellar atmospheres, the LTE cross sections are more appropriate and molecular ion abundances may be larger [34, 35]. We note that the LTE cross sections contribute to the bound-free opacity at longer wavelengths as illustrated in Figure 13. To aid in astrophysical models, all SH^+ photodissociation cross sections are posted on the UGA Molecular Opacity Project website§.

5. Conclusions

Using ab initio potentials and transition dipole moment functions, accurate cross-section calculations have been performed for the photodissociation of SH^+ through the transitions $2 ^3\Sigma^- \leftarrow \text{X } ^3\Sigma^-$, $3 ^3\Sigma^- \leftarrow \text{X } ^3\Sigma^-$, $\text{A } ^3\Pi \leftarrow \text{X } ^3\Sigma^-$, $2 ^3\Pi \leftarrow \text{X } ^3\Sigma^-$, and $3 ^3\Pi \leftarrow \text{X } ^3\Sigma^-$. The partial cross-sections have been evaluated from the vibrational levels $v'' = 0 - 19$ of the $\text{X } ^3\Sigma^-$ electronic state for wavelengths from

§ www.physast.uga.edu/ugamop

threshold to 500 Å. Assuming a Boltzmann distribution of rovibrational levels in the ground electronic state, so-called LTE cross sections have also been computed for all five electronic transitions for 1000-10,000 K. While it is found the $3\ ^3\Sigma^- \leftarrow X\ ^3\Sigma^-$ and $3\ ^3\Pi \leftarrow X\ ^3\Sigma^-$ transitions give the dominant cross sections near the Lyman limit, important contributions are provided by the $A\ ^3\Pi \leftarrow X\ ^3\Sigma^-$ for high rovibrational levels and, in the case of LTE, high temperatures particularly for longer wavelengths greater ~ 2500 Å.

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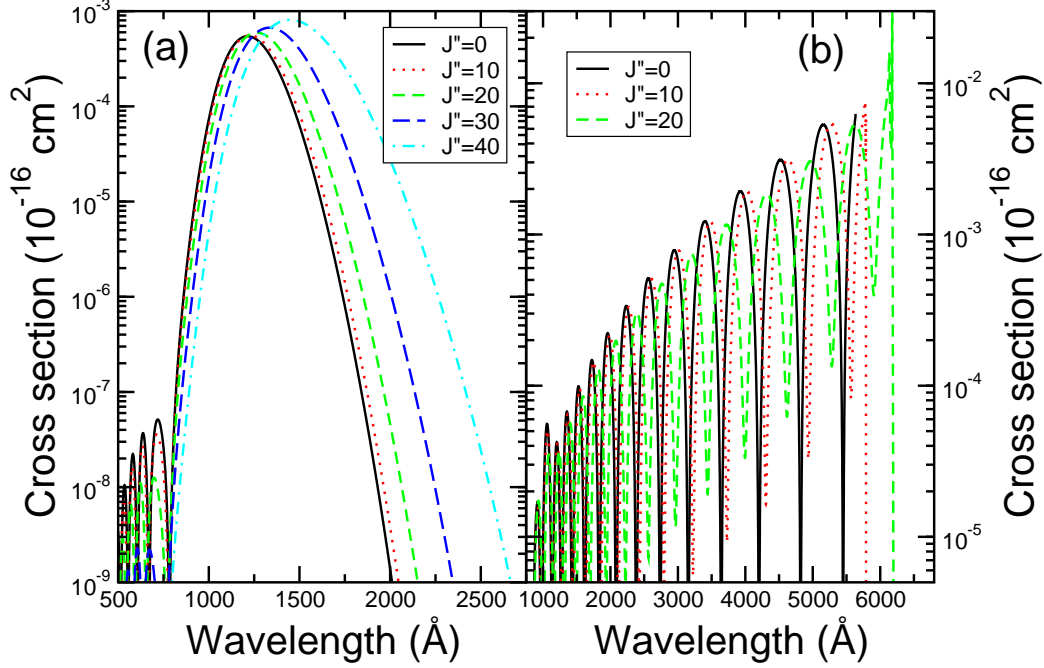


Figure 2. The computed partial SH^+ photodissociation cross-sections for the $2\ ^3\Sigma^- \leftarrow X\ ^3\Sigma^-$ rovibrational transition for (a) $v'' = 0$ and select J'' and (b) $v'' = 15$ and select J'' .

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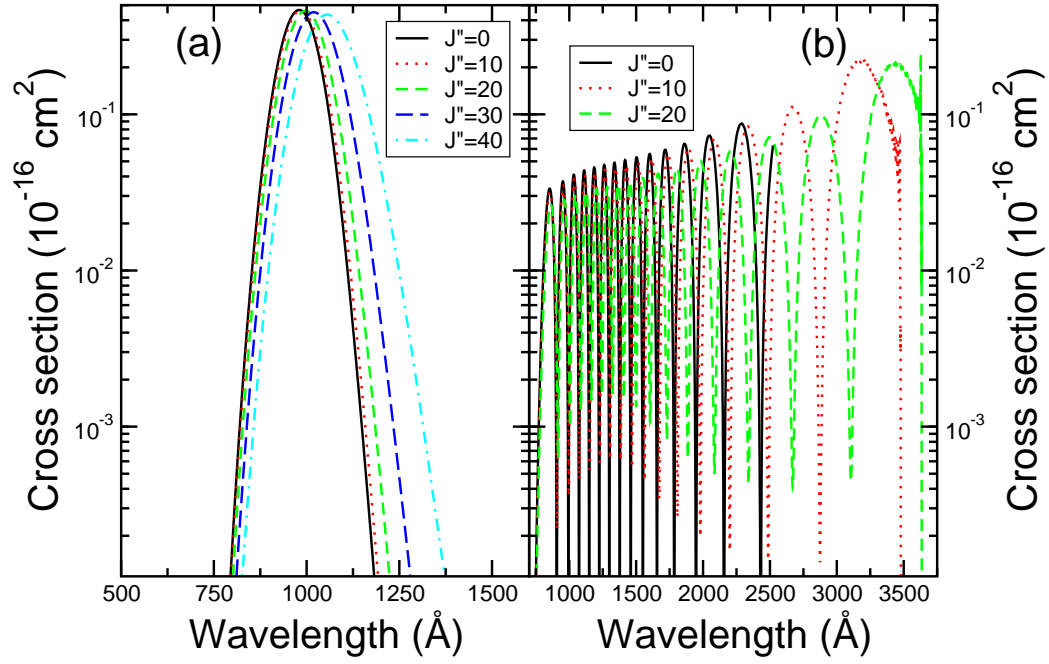


Figure 3. The computed partial SH^+ photodissociation cross-sections for the $3\ ^3\Sigma^- \leftarrow X\ ^3\Sigma^-$ rovibrational transition for (a) $v'' = 0$ and select J'' and (b) $v'' = 15$ and select J'' .

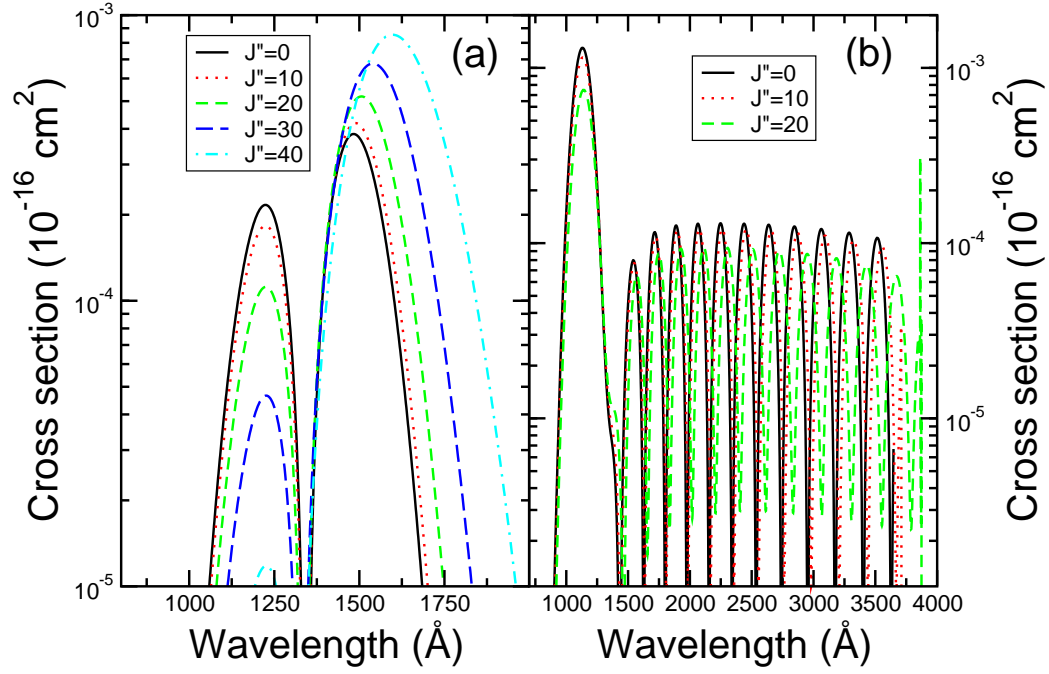


Figure 4. The computed partial SH^+ photodissociation cross-sections for the $2^3\Pi \leftarrow X^3\Sigma^-$ rovibrational transition for (a) $v'' = 0$ and select J'' and (b) $v'' = 15$ and select J'' .

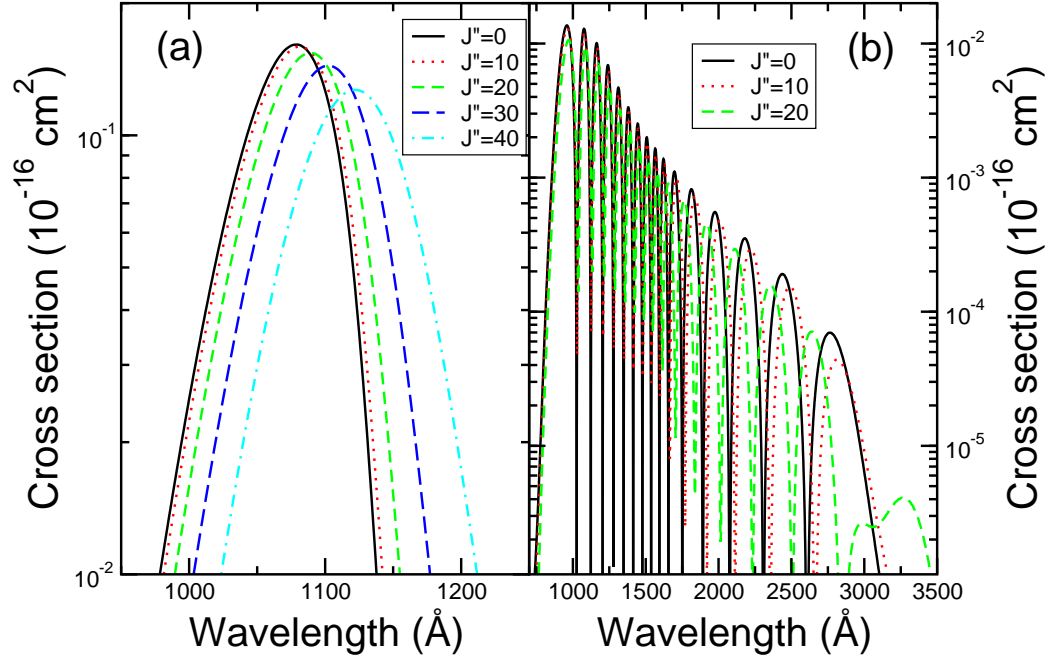


Figure 5. The computed partial SH^+ photodissociation cross-sections for the $3 \ ^3\Pi \leftarrow X \ ^3\Sigma^-$ rovibrational transition for (a) $v'' = 0$ and select J'' and (b) $v'' = 15$ and select J'' .

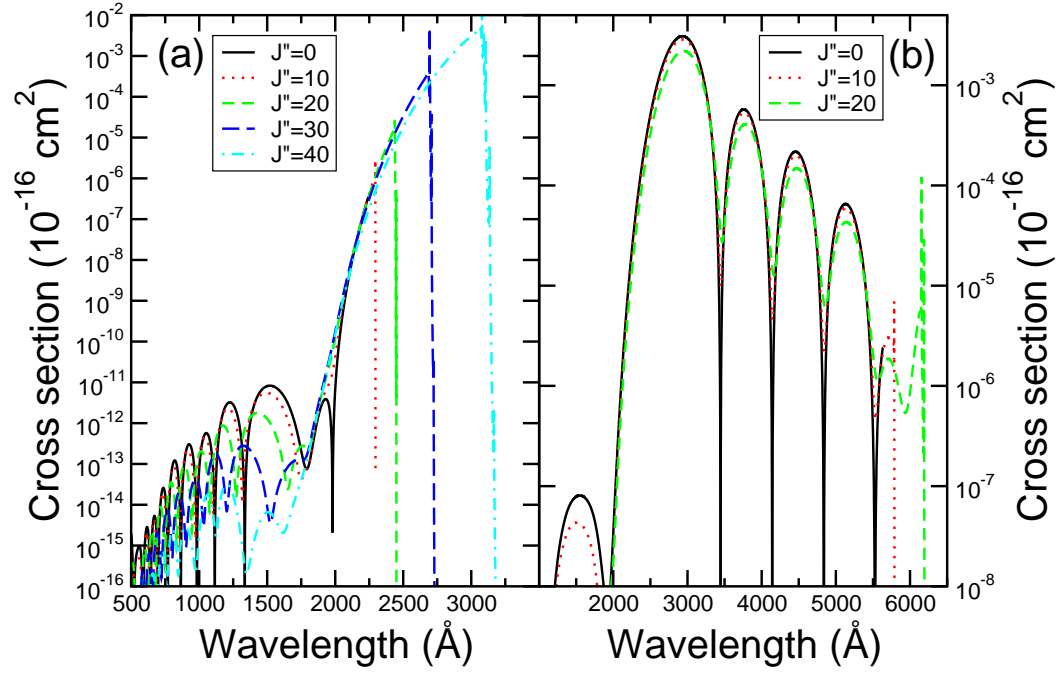


Figure 6. The computed partial SH^+ photodissociation cross-sections for the $A \ ^3\Pi \leftarrow X \ ^3\Sigma^-$ rovibrational transition for (a) $v'' = 0$ and select J'' and (b) $v'' = 15$ and select J'' .

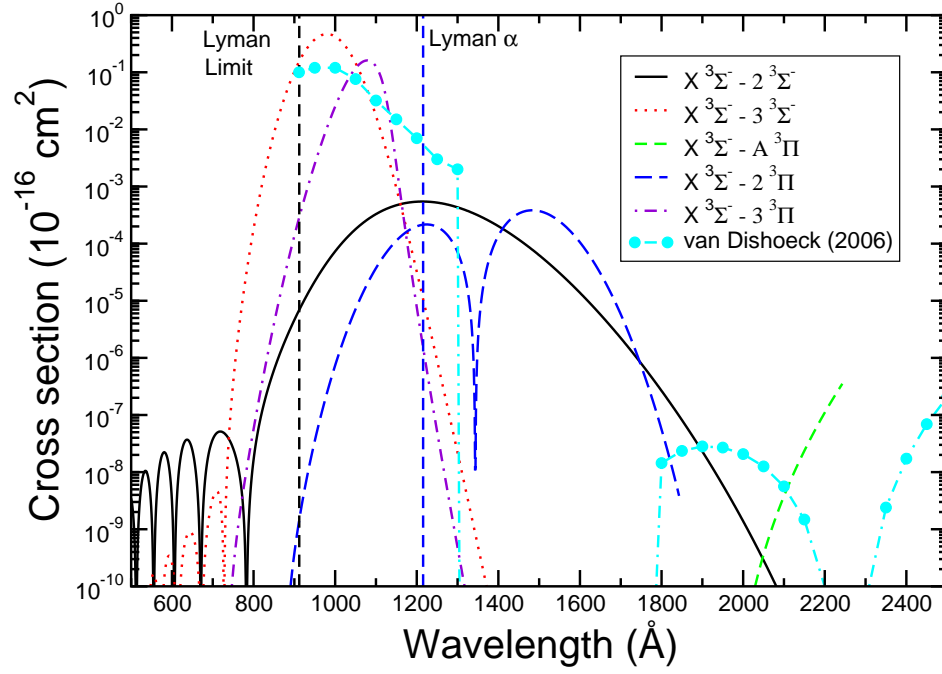


Figure 7. Comparison of SH^+ photodissociation cross sections for $v'' = 0$ and $J'' = 0$ with estimates from Ref. [32].

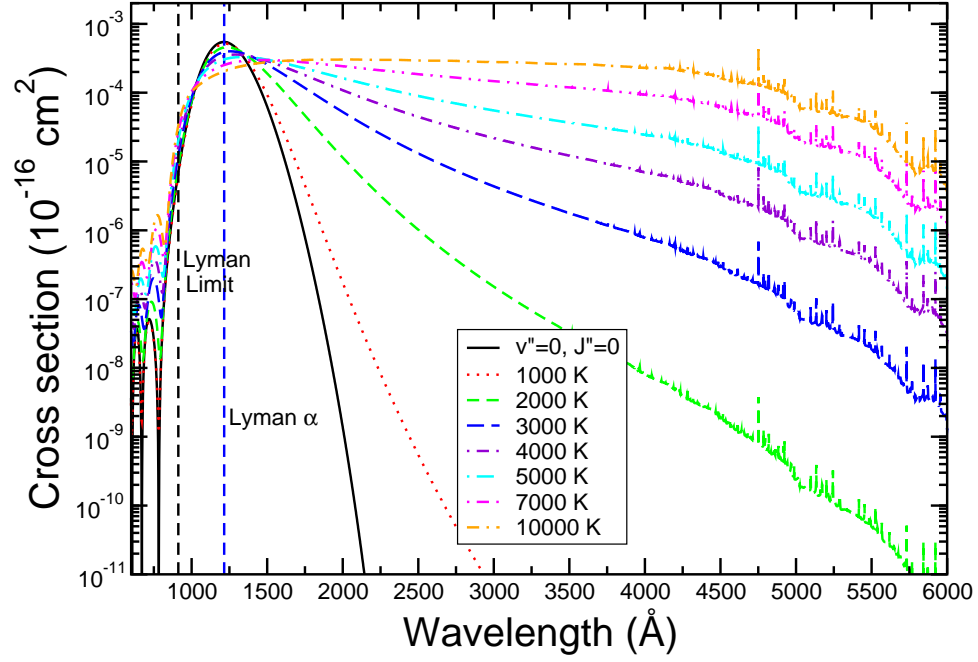


Figure 8. Total $SH^+ 2^3\Sigma^- \leftarrow X^3\Sigma^-$ LTE photodissociation cross section for temperatures from 1000 to 10,000 K. The $v'' = 0, J'' = 0$ partial cross section is also plotted for comparison.

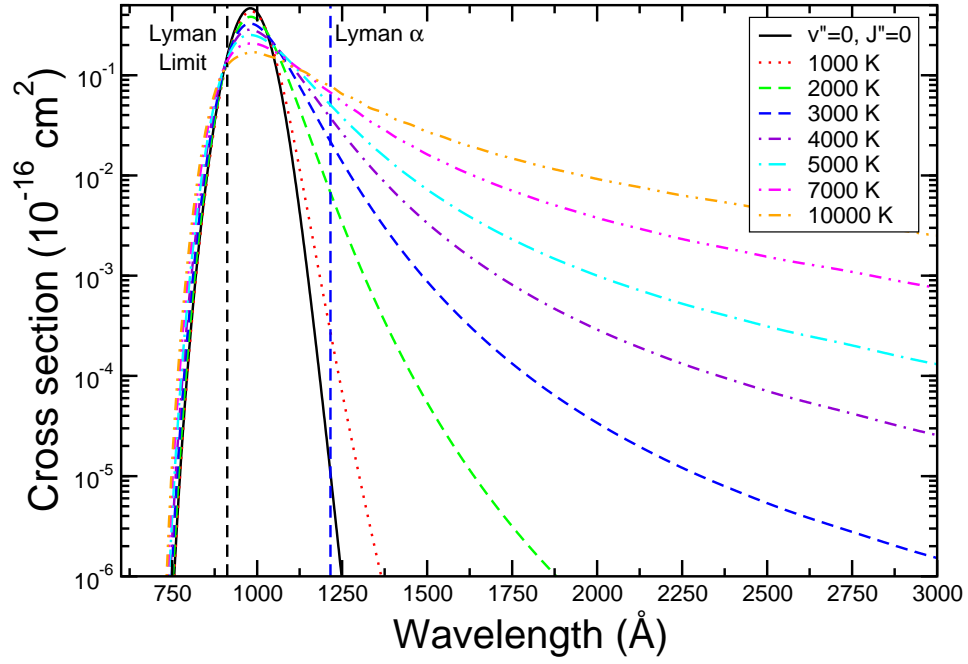


Figure 9. Total $SH^+ 3^3\Sigma^- \leftarrow X^3\Sigma^-$ LTE photodissociation cross section for temperatures from 1000 to 10,000 K. The $v'' = 0, J'' = 0$ partial cross section is also plotted for comparison.

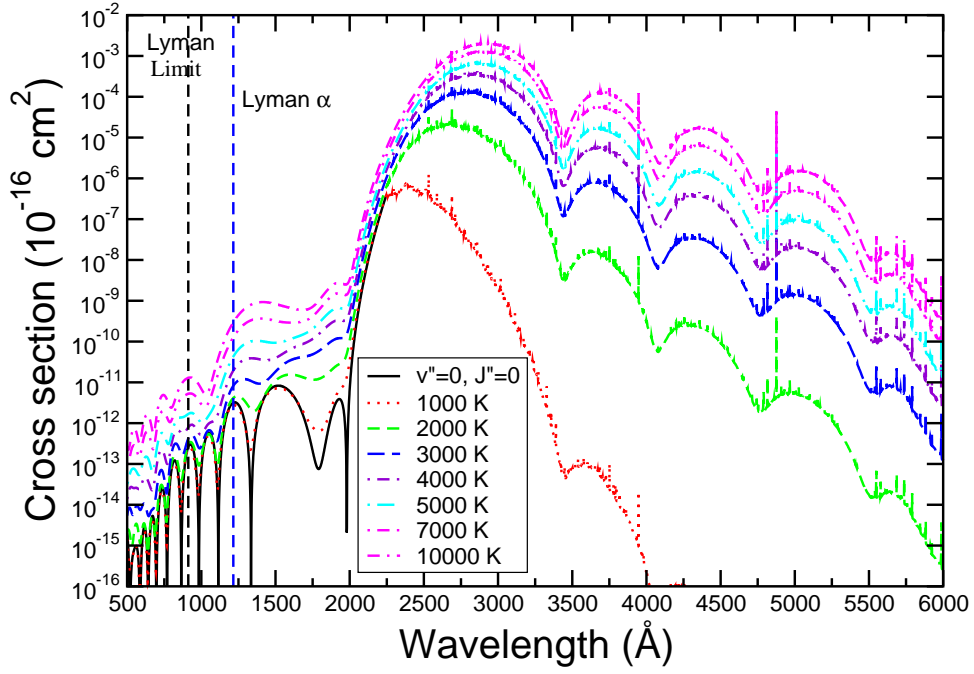


Figure 10. Total $SH^+ A^3\Pi \leftarrow X^3\Sigma^-$ LTE photodissociation cross section for temperatures from 1000 to 10,000 K. The $v'' = 0, J'' = 0$ partial cross section is also plotted for comparison.

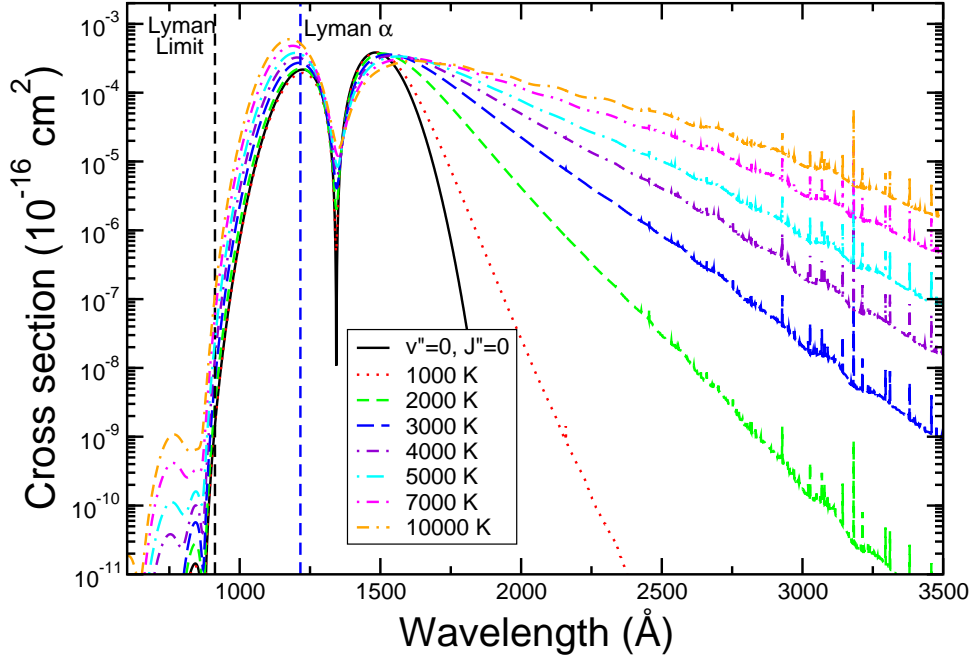


Figure 11. Total $SH^+ 2\ ^3\Pi \leftarrow X\ ^3\Sigma^-$ LTE photodissociation cross section for temperatures from 1000 to 10,000 K. The $v'' = 0, J'' = 0$ partial cross section is also plotted for comparison.

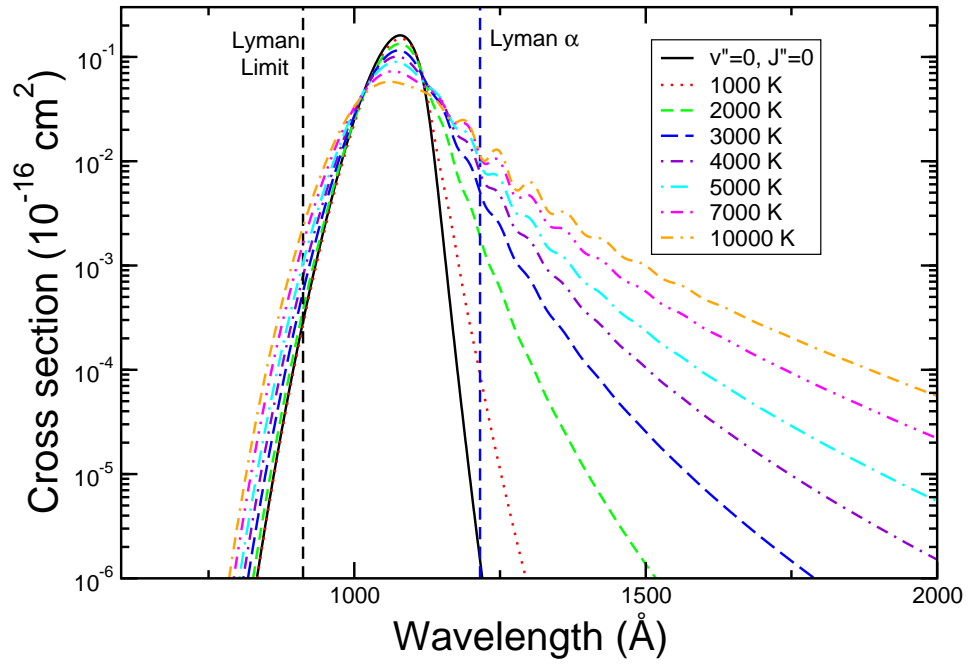


Figure 12. Total $SH^+ 3\ ^3\Pi \leftarrow X\ ^3\Sigma^-$ LTE photodissociation cross section for temperatures from 1000 to 10,000 K. The $v'' = 0, J'' = 0$ partial cross section is also plotted for comparison.

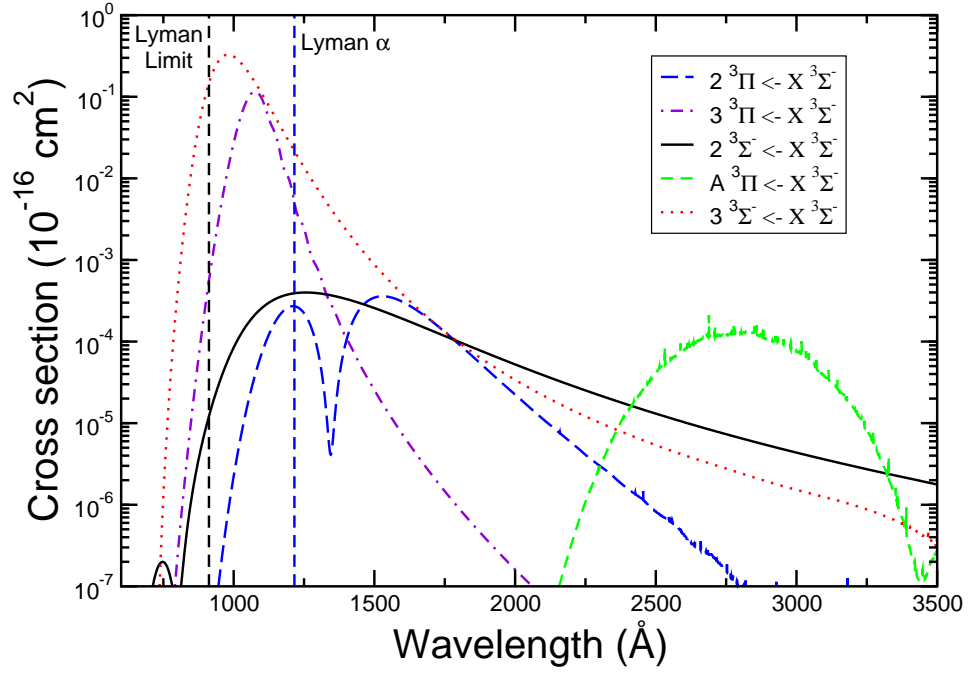


Figure 13. Total SH^+ LTE photodissociation cross section at 3000 K for all electronic transitions. Blackbody radiation curves (dotted lines) for various radiation temperatures are plotted for comparison (to be added).